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Once completed, the report should be submitted electronically to the User Office using the
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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

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Report:

The results presented in this report are on an experiment number 2-01-900 performed at dubble (BM26A) between 23rd and 27th September 2010. We employed energy resolved XAS as well as conventional EXAFS for studies Vox/TiO$_2$ and CoMoO$_4$ catalysts. The experiments were carried out at V K-edge and Co K-edge.

As for e-yield measurements we were not able to measure these catalysts. We spent considerable amount of time on getting detector to work. However, we were not successful in obtaining energy resolved XAS at V K-edge. The e-detector was saturated as soon as X-rays hit the sample.

We also performed fluorescence measurements at V K-edge on these catalysts. We collected several scans for each sample in order to improve signal to noise ratio. Samples were compressed into 20 mm diameter pellets. The concentrated samples were diluted with boron nitride. The contribution from TiO$_2$ was minimized by putting an aluminium sheet in front of fluorescence detector.

Though we did several runs for each sample, the EXAFS data for low concentrated samples (less than 6.3 w% of V$_2$O$_5$) are very poor quality as shown in Figure 1. In this plot are compared the EXAFS data for VO$_x$/TiO$_2$ catalyst containing 2 monolayer of VO$_x$ species prepared on TiO$_2$ powder support from Sigma Aldrich – black line (ALD-1.4), and the same TiO$_2$ powder support (Sigma Aldrich) which was washed in order to remove potassium impurities before being used for coating. The XANES parts of XAFS spectra at V K-edge for these two samples look identical. We can see a big pre edge feature similar to V$_2$O$_5$. Nevertheless,

we should be able to determine from this data the ratio of valence states for vanadium in the VOx/TiO$_2$ catalyst by linear combination least square fit of known spectra. Furthermore, the position of the XANES features in particular pre-edge or main edge is used to determine the vanadium valance state. V K-edge XANES spectra of different vanadium compounds are illustrated in Figure 2. These spectra will be used for obtaining information on the vanadium oxidation state and the coordination symmetry around the V absorber.
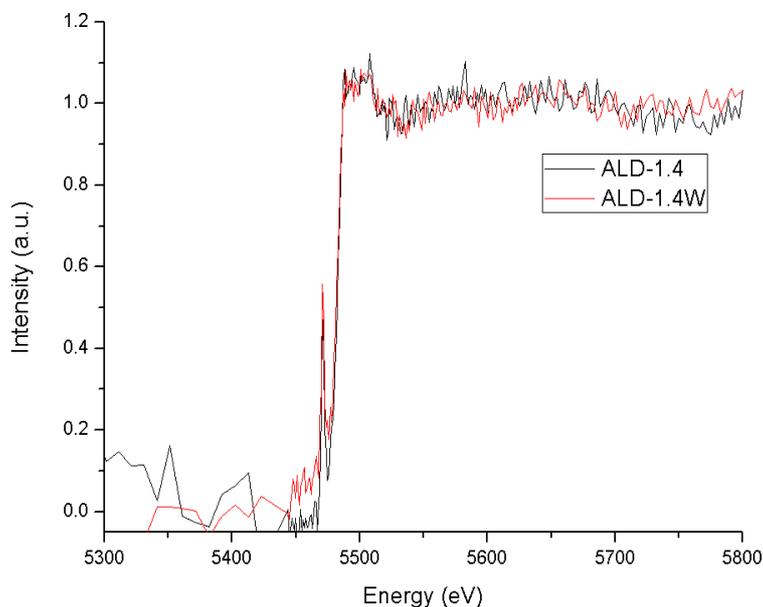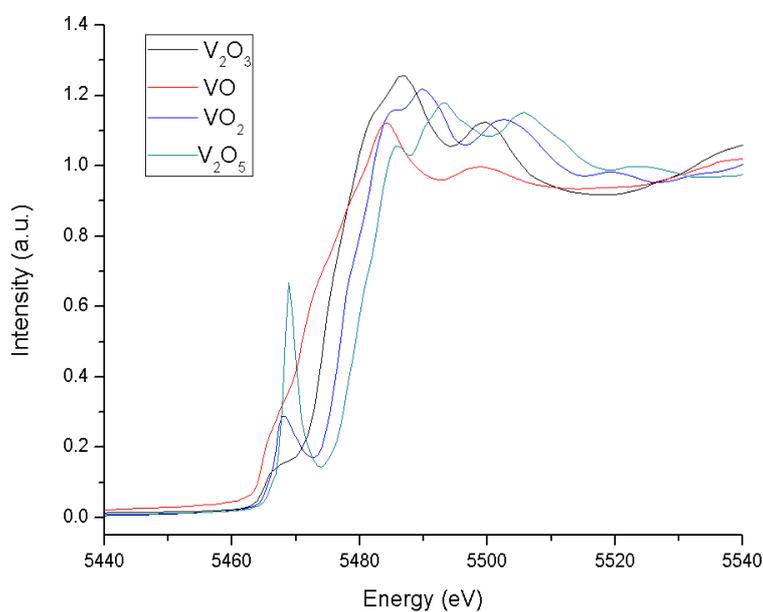

Figure 1V K-edge EXAFS forALD-1.4 and ALD1.4W.

Figure 2V K-edge XANES for V$_2$O$_3$ (black), VO (red), VO$_2$ (blue) and V$_2$O$_5$ (dark cyan).
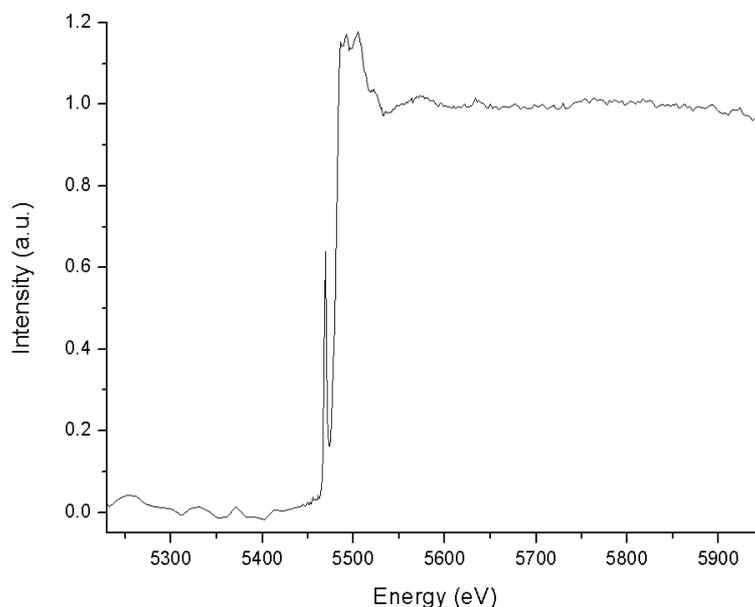
Figure 3V K-edge EXAFS for AA-7.5.

Figure 3 illustrating EXAFS data for VOx/TiO$_2$ catalyst prepared from Alfa-Aesar TiO$_2$ powder support which contains 7.5 w% V$_2$O$_5$ which is equivalent to 2.1 monolayer of VOx species. This XAFS data will be used for determination of bulk structure of catalyst as well as oxidation state. Unfortunately, we didn't manage to collect EXAFS data on Ti K-edge for VOx/TiO$_2$ catalyst prepared on TiO$_2$ powder support from Sigma Aldrich and Alfa Aesar.

We also performed measurements with e-yield detector at Co K-edge, since our last attempt was not successful. We looked at alpha phase of cobalt molybdate prepared hydrothermal method from cobalt acetate and cobalt nitrate. Powder was deposited on conductive carbon tape stuck on the brass holder. During measurements sample was inclined at 2.5^0 with respect to the incoming X-ray beam. In Figure 4 is shown typical pulse height distribution spectrum corresponding to last point of EXAFS scan obtained from measurements with e-yield detector.
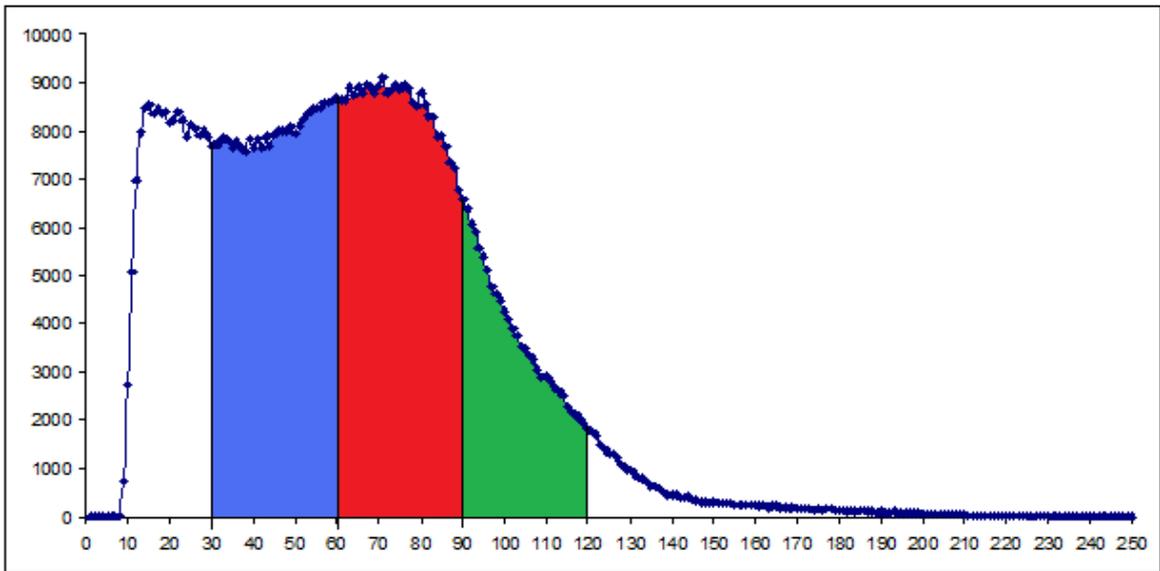
Figure 4The PHD spectra for alpha-CoMoO₄

An area under the PHD spectrum is divided into 3 different Auger electron energy regions found by experimenting. The energy region marked as blue corresponds to the partial electron yield (PEY) from the bulk - PEY1, while blue is PEY2 which is a mixture of the surface and bulk, and green one is coming from the surface of the catalyst. By integrating the area under the Auger electron energy regions, the EXAFS spectra (Figure 5) are obtained as function of depth of catalyst from the surface to the bulk. Looking at the XAFS part of the XANES spectra, the changes in the intensity can be observed.
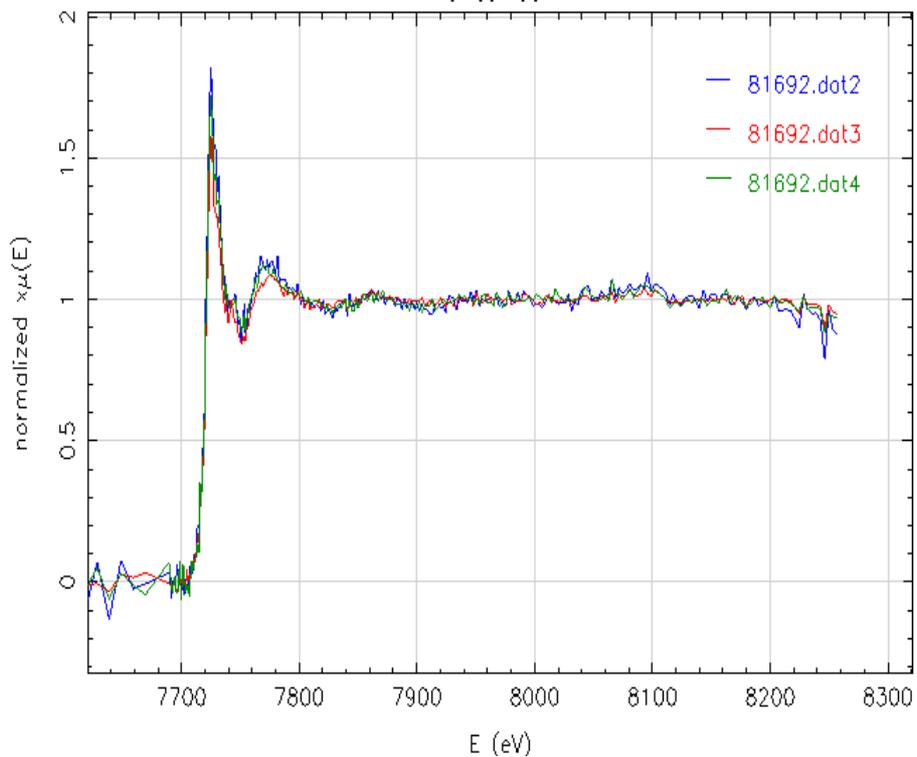

Figure 5 Co K-edge PEY spectra corresponding to different Auger electron energy region. The blue line is PEY1, red PEY2 and green PEY3.
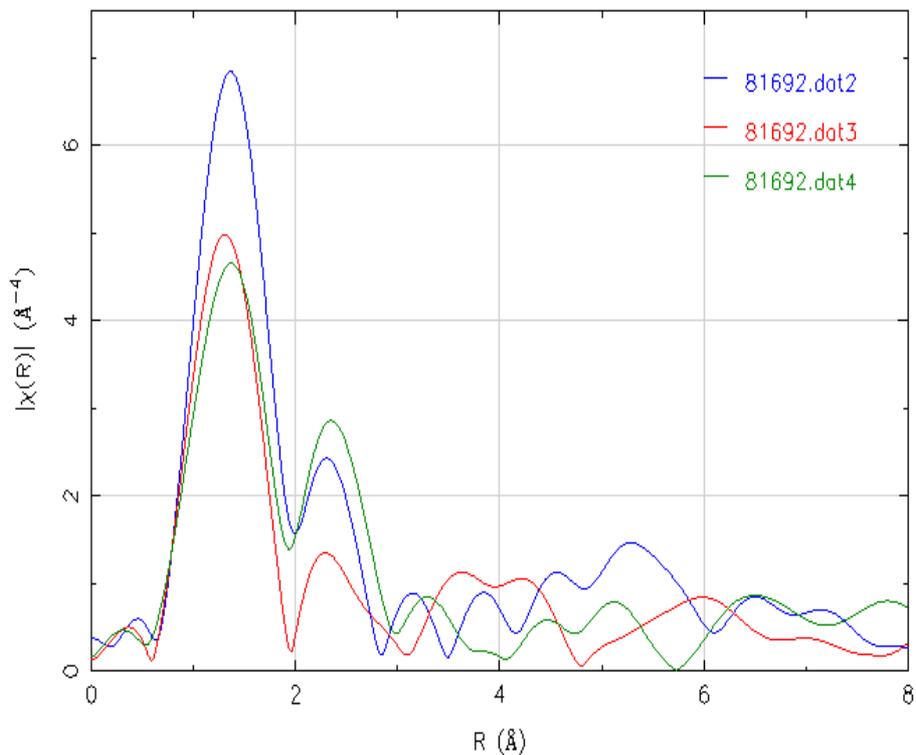
Figure 6 Fourier transformed PEY1-blue, PEY2-red and PEY3- green.

The Fourier transformed EXAFS for different partial electron yield spectra are shown in Figure 6. We can clearly observe changes in the magnitude of the first shell as function of the depth of the catalyst.

Conclusion

Our preliminary V K-edge XAFS results on VOx/TiO$_2$ catalyst should be sufficient for identifying valence state of vanadium. As for energy resolved XAS at Co K-edge we have shown that it is possible to distinguish between the bulk and surface structure of the catalyst by employing e-yield detector.